## COMMUNICATIONS

# Vibrational spectroscopy on single $C_{60}$ molecules: The role of molecular orientation

J. I. Pascual[a)]
*Fritz-Haber-Institut der Max-Planck-Gesellschaft. Faradayweg 4-6 14195 Berlin, Germany and Institut de Cíència de Materials de Barcelona-CSIC, Campus de la UAB E-08193 Bellaterra, Spain*

J. Gómez-Herrero
*Dpto. Física de la Materia Condensada. Universidad Autónoma de Madrid 28049 Madrid, Spain*

D. Sánchez-Portal
*Donostia International Physics Center (DIPC) 20018 Donostia, Spain*

H.-P. Rust
*Fritz-Haber-Institut der Max-Planck-Gesellschaft. Faradayweg 4-6 14195 Berlin, Germany*

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The excitation of a fullerene-cage vibrational mode by inelastic tunneling electrons has been observed on single $C_{60}$ molecules adsorbed on Ag(110). The vibration is assigned to the $H_g(\omega_2)$ mode. A critical enhancement of the inelastic signal was found on fullerenes oriented along one of their symmetry axis upon adsorption. In strong coincidence, those fullerenes maintain a resonance structure at the Fermi level that resembles the first unoccupied molecular orbital distribution of a free molecule, as determined by comparison with *ab initio* calculations. The degree of symmetry of the adsorbed fullerene is found to be crucial for resonant mechanism of vibrational excitation. We also propose that mode degeneracy splitting may reduce mode detection. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1524155]

Inelastic electron tunneling spectroscopy (IETS) is a powerful technique to obtain average vibrational information on condensed molecular species.[1] Following the discovery of scanning tunneling microscopy (STM) and spectroscopy (STS), it was soon proposed that the combination IETS-STM would provide vibrational information resolved on single molecules.[2,3] Since its first experimental demonstration[4] a number of detailed studies have addressed several fundamental aspects related with both excitation and detection of vibrational modes in the IETS-STM configuration. A variety of experimental observations that go beyond a simple picture of mode excitation by inelastic tunneling electrons describe the complexities behind the excitation mechanisms. Some of these include negative signal,[5] fanolike line-shape,[6] conformational changes of the adsorbate tuned by the excitation of vibrations,[7] or the activation of ''hidden'' modes on species slightly perturbed.[6,8] In some of these works, the molecular symmetries were pointed out as having a significant role in the excitation mechanisms.[5,6,8] In particular, the symmetry of vibrational modes and electronic resonances of an adsorbate seems to give rise to selection rules for vibrational mode detection in IETS-STM.[9]

Here we work with a molecular specie with high symmetry: $C_{60}$. This molecule has become very well studied in both solid state and adsorbed thin layers.[10] A great part of the interest on these fullerenes comes from the icosahedral ($I_h$) symmetry of the molecular cage, which defines highly degenerated vibrational and electronic eigenmodes. When $C_{60}$ is adsorbed on a surface the structure of the free molecule remains fairly unaltered.[11] STM resolves the molecular orientation[11,12] and its electronic configuration[13] at the single molecular level, both related with fundamental aspects of the local molecular adsorption properties.[14]

It is a challenge to extend our inelastic STS (ISTS) studies to this system, aiming for fundamental understanding about the role of such large degeneracies on molecular vibrational eigenmodes. In this work we report the finding of a clear vibrational fingerprint in the ISTS spectra acquired on single $C_{60}$ molecules adsorbed on Ag(110). The detected mode is associated with an internal vibration of the molecular cage, thus involving purely C–C bonds in a collective deformation of the molecular cavity. The fundamental significance of this finding arises from the surprising dependence of the mode detection on the molecular orientation on the surface.

The acquisition of ISTS spectra requires long time measurements, and high energy resolution.[15] Consequently, our experiments have been performed at a temperature of $\sim 4.5$ K, in a scanning tunnelling microscope sited in a ultra–high vacuum chamber.[16] A PtIr tip was used in the experiments. Lock-in modulation techniques were used for the detection of the $2\omega$ signal (here referred as vibrational or inelastic signal). Commercially available high purity $C_{60}$ powder was degassed for several hours previous to deposi-

a)Electronic mail: pascual@icmab.es

 

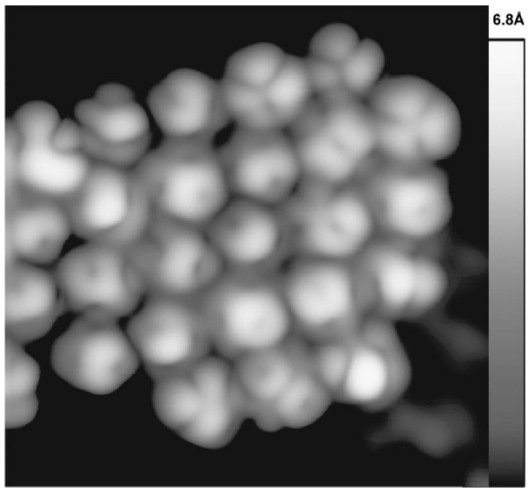


FIG. 1. (a) STM image of a $C_{60}$ island on Ag(110). ($6.1\times6.1\ \mathrm{nm}^2$, $I=1.0$ nA, $V_s=-0.1$ V.)

tion of submonolayer amounts on a Ag(110) surface using a radiatively heated crucible. The Ag(110) crystal was cleaned using repetitive cycles of $Ar^+$ sputtering (1 KeV) and annealing ($\sim$750 K).

On Ag(110), post-deposition annealing promotes nucleation in ordered self-assembled molecular islands of $C_{60}$,[17] but usually also causes a particular molecular orientation to predominate. Since we are interested in a study of ISTS spectra as a function of molecular symmetry, we avoided post-deposition annealing in order to promote adsorption on several metastable states with different orientations of the molecular cage.

STM topographies of the sample (Fig. 1) confirm that, even though the molecules still assemble in islands, they show no well defined structural arrangement, far from the $c(4\times4)$ observed by David *et al.* for post-annealed samples.[17] A closer look into one of these islands reveals that the intramolecular structure is clearly resolved within the fullerene cages. These structures can be used to determine the molecular orientation,[11,12] evidencing the existence of various stable adsorption configurations characterized by different molecular cage orientations.

In Fig. 1, it is also evident that some particular species show an internal structure which resembles one of the symmetries of the free molecule. These fullerenes are expected to keep part of their free molecular identity upon adsorption.[11] Thus, the internal structure in STM images with low sample bias ($V_s$) may be heuristically compared with the spatial shape of the orbital density $|\Sigma\psi_i(\mathbf{r})|^2$ for any combination of free-molecule MO's $i$.[11] Figure 2 shows a comparison of the STM image of two of these fullerenes with the lowest unoccupied molecular orbital (LUMO) density obtained from *ab initio* simulation of the free molecule. This is the only molecular orbital that reproduces the experimental internal structure in every case. In Figs. 2(a) and 2(b), the agreement is obtained after representing the LUMO density with the $C_3$ and $C_2$ symmetry axis respectively pointing perpendicularly to the figure. It must be then inferred that this is indeed the molecular orientation, and hence, the symmetry element maintained upon adsorption. The azimuthal orientation of the

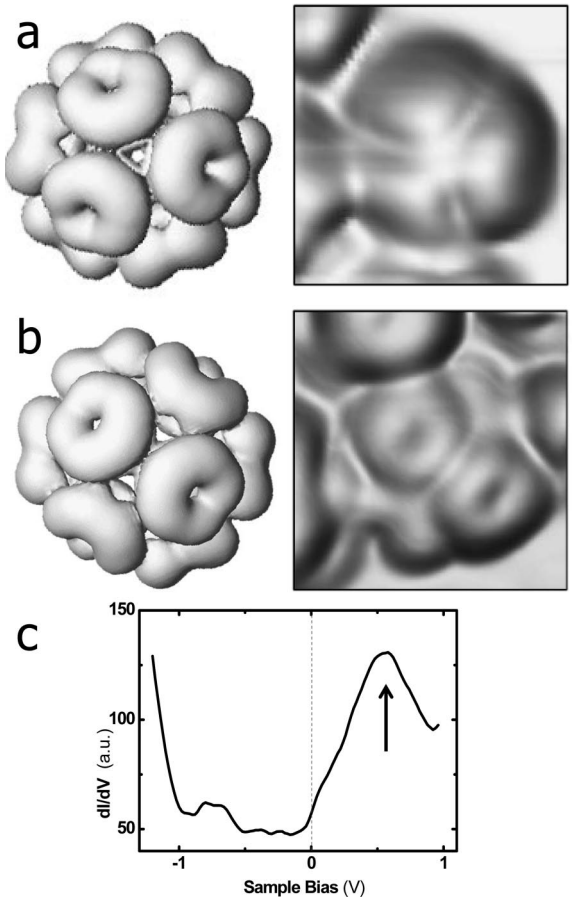


FIG. 2. (a,b) STM images of $C_{60}$ molecules (right) compared with calculations of isosurfaces of the squared LUMO of a free $C_{60}$ (left). Both experimental and simulated images are laterally illuminated in the figure. The calculations were performed with the SIESTA program (Refs. 29, 30), based on density-functional theory, in the local-density approximation, using norm-conserving pseudopotentials and a basis set of atomic orbitals, including double-$\zeta$ $s$ and $p$ orbitals, and single-$\zeta$ $d$ orbitals for polarization. In the free molecule, the LUMO is three-fold degenerated. (c) $dI/dV$ vs $V_s$ spectrum on a single $C_{60}$ molecule. The spectrum is average of six bias voltage scans (2 sec/scan). The arrow points to the LUMO-derived peak. [(a) and (b) $1.3\times1.3\ \mathrm{nm}^2$, $I=1.0$ nA, $V_s=-0.1$ V, (c) (set-point) $I=0.4$ nA, $V_s=0.5$ V.]

molecules can also be inferred from the comparison shown in Fig. 2, since the experimental images reproduce the characteristic rings found in the LUMO density calculations, representing regions of larger charge density located around the pentagonal faces of the molecular cage.

The intramolecular structure, like the examples shown in Fig. 2, is independent of the bias polarity at values close to $E_F$. This is an indication of the existence of a LUMO-derived resonance dominating the electronic states at energies around $E_F$.[18] $dI/dV$ spectra show the position of this unoccupied resonance at 0.5 eV above $E_F$, intrinsically broadened presumably by the interaction with the surface, and with its lower energy tail extended below $E_F$ [Fig 2(c)]. The population of LUMO-derived states at $E_F$ reflects the nature of the adsorption bond, consisting in a predominantly ionic type of charge transfer into the LUMO.[19] Thus, these molecular-derived resonances play a very significant role in the electronic transport through the tunnel junction at ener-

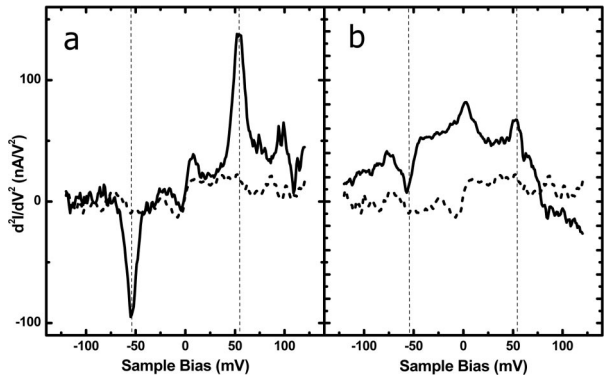


FIG. 3. Comparison of ISTS spectra measured consecutively on two neighboring $C_{60}$ molecules. The dashed plot corresponds to the spectrum acquired on the bare silver surface. Each spectrum is the average of six bias voltage scans (25 sec/scan). In (a), the peak at 54 mV ($-54$ mV) represents a normalized change in conductance of 9% (8%). ($I=1.6$ nA, $V_s=0.5$ V, $V_{ac}=5$ mV rms at $f_{ac}=341$ Hz.)

gies around $E_F$, and probably are strongly involved in the excitation of molecular vibrations.

The vibrational structure of a free $C_{60}$ molecule shows by 46 distinct excitations with energies ranging from 33 to 195 MeV. Most of the modes are highly degenerated, accounting for a total of 174 internal vibrations of a molecular cage with icosahedral symmetry. On an adsorbed specie, the energy of the modes may shift, and their degeneration may split, reflecting several aspects of their interaction with the surface, such as the chemical interaction,[20] the effect of the crystal potential and/or cage deformations.

In ISTS, the vibrational structure of single molecules is resolved by measuring the second derivative of the tunneling current respect to $V_s$, $(d^2I/dV^2)$, an experimental procedure similar to that used in IETS,[1] and reported in detail previously.[4,15] $d^2I/dV^2$ spectra measured on top of a $C_{60}$ molecule [Fig. 3(a)] reproduce a narrow peak located at a positive bias value of 54 mV, which is accompanied by a narrow dip approximately at the same value in the negative polarity. Such symmetric location of both peaks around the 0 bias axis is intrinsically associated with the enabling of inelastic scattering phenomena at the energy of a particular vibrational excitation. Therefore, the peaks in Fig. 3(a) are attributed to the excitation of a molecular vibrational mode with an energy of 54 MeV. Occasionally, small variations in the peak position are resolved in the window of $\pm 3$ MeV around this value. Although the origin of these variations is not well understood, they are likely to be related to local changes in the nature of the adsorption bond.

Regarding the assignment of this vibration, we note that only one out of the 46 internal modes of the $C_{60}$ cage has energies values around 54 MeV (i.e., 432 $cm^{-1}$): the $H_g(\omega_2)$ mode, corresponding to a ''gerade'' breathing of the molecular cage with larger radial component along the $C_{5v}$ symmetry axis.[10] In the free molecule, this mode is 5-fold degenerated. Since the modes with $H_g$ symmetry are Raman active, the frequency of $H_g(\omega_2)$ (431 $cm^{-1}$) is pretty well determined from both experiment and theory.[21] On a silver surface, the mode frequency is slightly shifted down to 419 $cm^{-1}$ (52 mV),[22] making our assignment quite unequivocal.

Surprisingly, a vibrational spectrum like that in Fig. 3(a) is not observed on all the molecules, even for equal measurement conditions. Many of the fullerenes show rather faint features, hardly resolved from the background [Fig. 3(b)]. Such local changes in the observation of a vibrational mode offer the possibility to investigate mechanisms related to the so-called ''missing'' modes in ISTS spectra. Previous experimental studies have reported the observation of ''nonactive'' modes in the tunnelling spectra of benzene after partial molecular fragmentation,[8] and local distortion of their adsorption configuration.[6,23] The use of functionalized tips may also enable the observation of additional modes in the ISTS spectra.[24] The lack of signal from some molecular modes has been theoretically assigned to a cancellation of the inelastic signal due to electronic interference mechanisms of the inelastic[25] and/or elastic channels.[26] These processes are enabled by internal vibration–electronic (vibronic) coupling, and therefore, are strongly dependent on the electronic structure of the adsorbate.

To shed some light on the origin of this lack of vibrational signal on some $C_{60}$ molecules, we have acquired the spatial distribution of $d^2I/dV^2$ on fullerene islands. With this procedure, we can precisely determine the location where the excitation of the $H_g(\omega_2)$ vibrational mode is preferentially detected within the molecular cavity.[27] One of these vibrational maps is shown in Fig. 4(b), measured at a tunnel bias of 56 mV, around the onset of this vibrational mode. For comparison, we also show spectroscopy maps of the same region acquired at sample bias values of 40 mV [Fig. 4(a)] and 70 mV [Fig. 4(c)]. It is important to note that the ''bright'' features in Fig. 4(b) represent an increase in the $d^2I/dV^2$ signal of more than 2 times respect to the same location in Figs. 4(a) and 4(c). By this comparison, we demonstrate that the enhanced structure in the $d^2I/dV^2$ map of Fig. 4(b) arises from local excitations of molecular vibrations, and not from electronic or topography components, which would be rather similar for the three bias values.

Figure 4(b) shows that, in agreement with their random rotational geometry, many fullerenes present no well-defined intramolecular vibrational patterns. Weak increments of $d^2I/dV^2$ can be randomly detected at small locations of about 5 $Å^2$ within a molecular cage. Only on some of the fullerenes the inelastic signal is clearly larger, thus corresponding to those molecules where clear peaks are observed in the vibrational spectrum. Interestingly, the patterns on these molecules resemble partly the symmetries of the molecular icosahedral cage. In the figure, the molecules labeled as $C_3$ and $C_2$ show patterns consisting of three and two lobes, respectively. The shape of these internal structures can be directly compared with the shape of the LDOS for the LUMO derived resonances, shown in Fig. 2, and thus related to a particular molecular orientation. Furthermore, we may locate the lobes representing higher inelastic signal at the pentagons of the icosahedral cage, where charge density *rings* are centered. Therefore, this spectroscopic maps correlate the enhancement of vibrational signal with the existence of remanent symmetries of the adsorbed icosahedral cage.

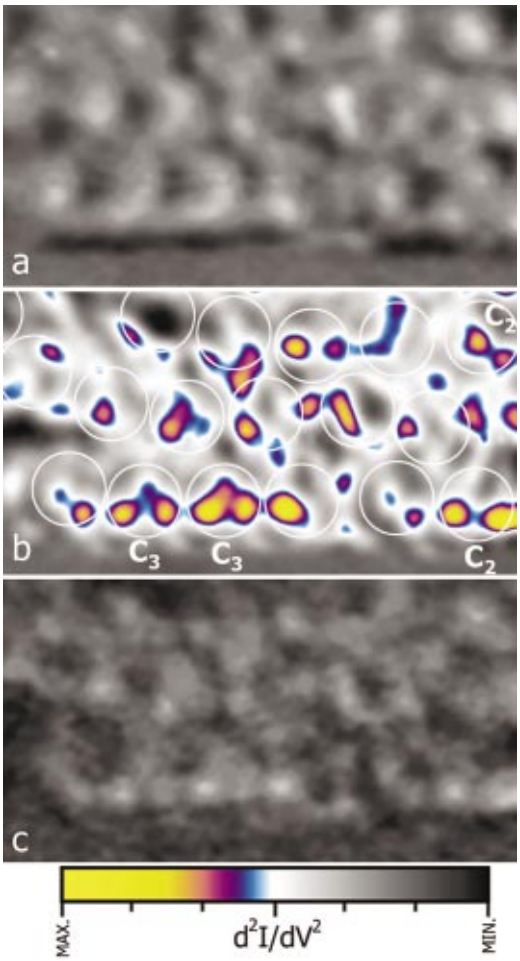


FIG. 4. (Color) Closed feedback $d^2I/dV^2$ maps of part of a $C_{60}$ island measured consecutively at (a) $V_s=40$ mV, (b) 56 mV, and (c) 70 mV. A critical enhancement of the signal is observed in (b), specially on some small locations within the molecular cage. White circles help to locate the position of the molecules in the corresponding topography image. ($I=1.6$ nA, $V_{ac}=6$ mV rms at $f_{ac}=941$ Hz).

Resonant mechanisms of vibrational excitation are probably intrinsically related to the signal enhancement on those fullerenes with some degree of orientational symmetry. It is widely accepted that molecular resonances dominate inelastic tunneling scattering processes on several smaller adsorbates.[3,5] Figure 2 resolves the dominant resonance distribution of LUMO derived states around the molecular pentagons, in coincidence with the regions of observation of maximal inelastic signal. Due to their specific spatial shape a strong vibronic coupling of both LUMO and $H_g(\omega_2)$ states is expected, and would explain the predominance of this mode in the ISTS spectra, as well as the enhancement of the vibrational signal whenever both remain partly unaffected from symmetry reduction mechanisms. Coupling of some specific vibrational modes with LUMO resonant tunneling was also eluded in previous IETS experiments to explain unusual effects on the intensities of their vibrational bands.[28]

Besides, the origin of such signal enhancement on fullerenes keeping some degree of symmetry upon adsorption may be related to the vibrational structure of the molecule itself. The $H_g(\omega_2)$ mode in the free molecule is 5-fold degenerated. On the surface, the degeneracy may be lifted as a consequence of the adsorption (crystal field splitting, deformations of the molecular cage or even a charge transfer into molecular orbitals). For molecules in a nonsymmetric orientation, degeneracy splitting, and subsequent mode mixing, may be so extensive that the observation of clear vibrational features in the ISTS spectra is suppressed. Only in those cases where some molecular symmetry survives upon adsorption, as it is the case shown in Fig. 2, some mode degeneracy remains, leading to a detectable contribution in the inelastic signal.

The nature of the electronic molecular resonances around $E_F$, which determines the vibrational mode primarily excited, and the existence of a surviving symmetry on the adsorbed specie, which determines magnitude, provide detection selection rules based on intrinsic properties of the adsorbed molecule. The determination of their extent would require further theoretical calculations and experiments where the nature of the molecular resonances at $E_F$ is tuned by choosing different substrates and/or adsorption temperatures.

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